ONTARIO
MINISTRY OF THE ENVIRONMENT

VOLATILE ORGANIC COMPOUNDS MONITORING NETWORK

STANDARD OPERATING PROCEDURES AND TECHNICAL MANUAL

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PREFACE

Airborne chemicals exist in particulate and vapour and organic and inorganic forms. Organics are of particular concern due to their complexity and variety of potential toxic effects, including carcinogenicity. Over the past few years the Organic Vapour Sampling Committee of the Ontario Ministry of the Environment has developed methods for measuring a number of volatile organic compounds (VOCs) in ambient air. The finalized measurement method is now being incorporated into a provincial network the results from which will provide a sound basis for hazard assessment and control action.

Specifically, the objectives of the program are:

1) To monitor ambient levels of targeted volatile organic compounds at selected urban and rural sites in Ontario in order to assess health impacts on the population.
2) To determine monthly, seasonal, and annual trends of volatile organic compound concentrations in the province of Ontario in order to assess the effectiveness of abatement programs.

Benefits of a province-wide VOC monitoring network include 1) comparison of typical urban and rural sites; 2) identification of problem areas

based on anomalously high VOC concentrations; 3) generation of a historical data base for ambient air which may later be used in conjunction with personal monitoring and indoor air monitoring to characterize the total inhalation exposure of the population of Ontario; and 4) comparison with other agencies for equivalency.

This manual describes the standard operating procedures for the network and should be used in conjunction with the Quality Assurance Plan. The manual is based on: 1) results from in-house developmental work; 2) guides, papers, and reviews; 3) internal correspondence from network operations; and 4) equipment instruction manuals. Input from regional personnel who operate the samplers and laboratory personnel who analyze the samples is gratefully acknowledged.

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1.0 THE VOLATILE ORGANIC COMPOUND SAMPLER

1.1 General Description

The volatile organic compound sampler consists of several off-the-shelf components assembled into a reliable, easy to use package. True VOCs do not exist in the particulate phase and thus the sampling equipment must reflect the requirement for collecting gaseous phase compounds. As an upstream particulate filter is not necessary, the sampler draws air from the sampling manifold straight onto a two-stage sorbent cartridge where volatile species are trapped for analysis by thermal desorption and GC/MS or GC/FID. The upstream sorbent is Carbotrap and the downstream sorbent is Carbosieve. When desorbing the collected sample, the air flow is reversed. Flow rate is controlled by a mass flow controller. A digital readout is used to set the flow rate for each cartridge since individual cartridges will have slightly different flow resistance due to variable sorbent volumes and packing characteristics. The mass flow controller is protected by an in-line particulate filter. An elapsed time indicator is used to measure the total time that the sampler operated. This provides an easy check on the sampler timer which controls the on/off function of the sampling train.

1.2 Components of the Sampling Train

The individual components of the sampling train are described below beginning at the upstream end of the sampling train (the sorbent cartridge) and

proceeding downstream, ending with the on/off timer and the elapsed time indicator.

1.2.1 Sorbent Cartridge

The sorbent cartridge itself is a 100 mm long by 10 mm (o.d.) borosilicate glass tube. Into this tube two different sorbents are packed in lengths of approximately 30 mm separated by a quartz wool layer. During sampling, the upstream sorbent is Carbotrap B (20/40 mesh) and the downstream sorbent is Carbosieve S (60/80 mesh).

1.2.2 Particulate Filter

The purpose of the downstream particulate filter is to protect the mass flow controller from any stray particles that may come through the sorbent cartridge or, possibly, off the quartz wool plugs used to pack the sorbents into the glass cartridge. The filter itself is a Millex-FG_{50} unit consisting of a polypropylene housing and filter support screens with an unlaminated, 50 mm diameter, 0.2 μm PTFE membrane sandwiched between the support screens.

1.2.3 Flow Measurement

Flow Measurement is accomplished using a two-part system consisting of a mass flow controller and a digital readout. The mass flow controller is a Tylan Model FC-280 calibrated at the factory for 0-50 ml air. The digital readout

powers the mass flow controller and, using a trim pot on the face of the instrument, is used to set the mass flow controller for the desired flow rate. The digital readout displays flow to a tenth of a ml.

1.2.4 Pump

The pump currently in use is a metal bellows type which runs off AC power. This particular unit is compact but rather expensive. Virtually any AC-powered pump should be capable of drawing the required 25 ml/min.

1.2.5 Timer

The timer is used to set the sample-on day and time and the sample-off day and time. The timer is a commercially available "Micronta" timer with a battery back-up to retain information in the event of a power failure. As an added precaution, an elapsed time indicator is also used to measure the total time that the sampler operated.

The sampling components are assembled as shown in Figure 1.1. The glass sampling port at the upstream end of the cartridge fits into the sampling manifold. The individual components are shown in Figures 1.2 through 1.4 inclusive (1.2 cartridge; 1.3 filter/flow controller/digital readout/ elapsed time indicator; 1.4 timer/pump).

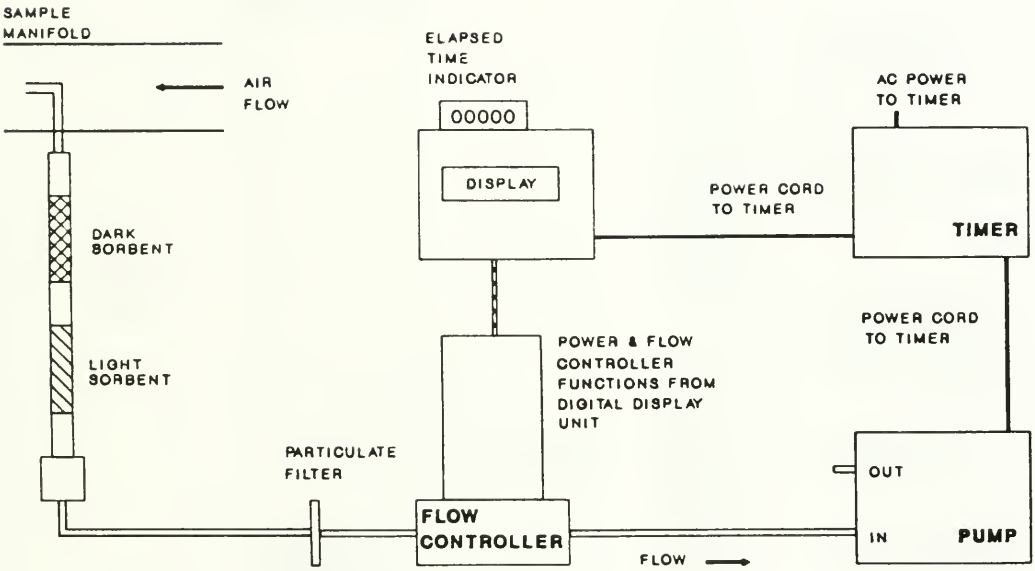


FIGURE 1.1. SCHEMATIC DIAGRAM OF ASSEMBLED SAMPLING TRAIN

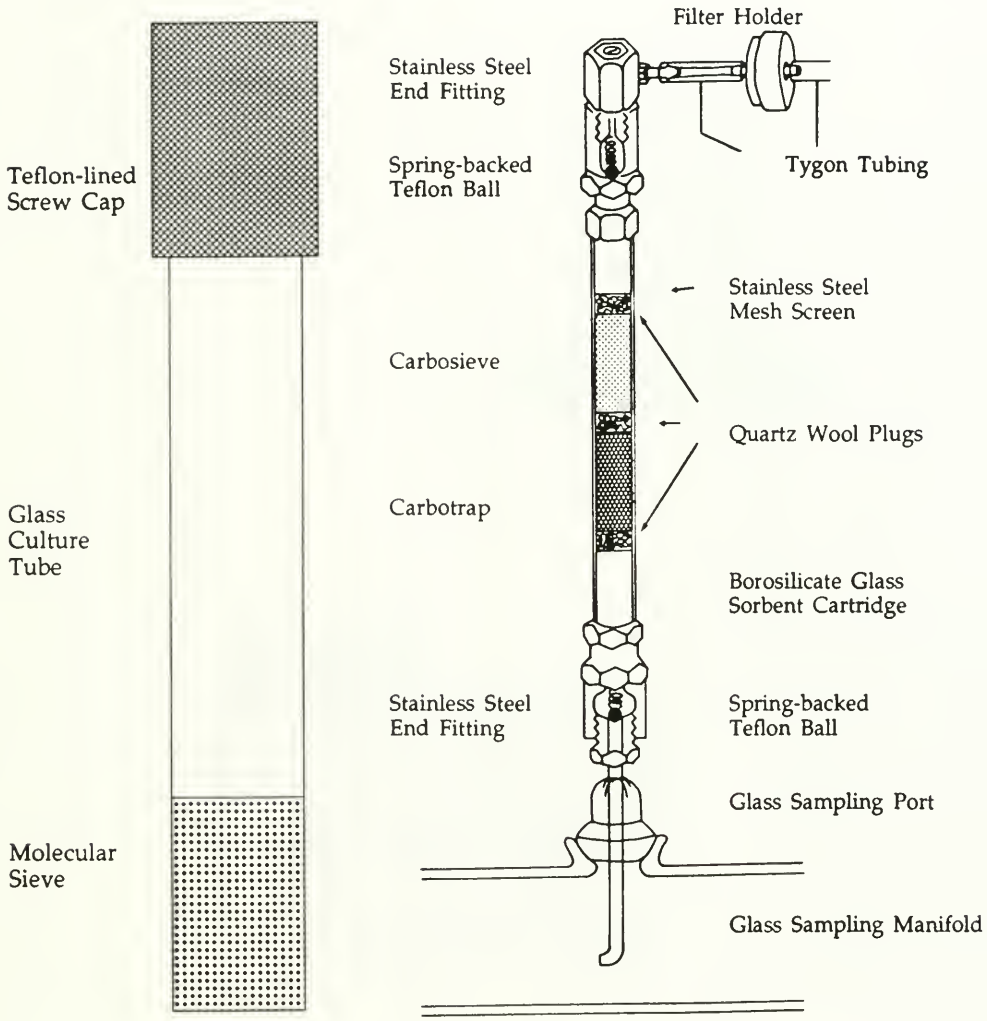


FIGURE 1.2. THE ADSORBENT CARTRIDGE AND SHIPPING TUBE

(Not to scale)

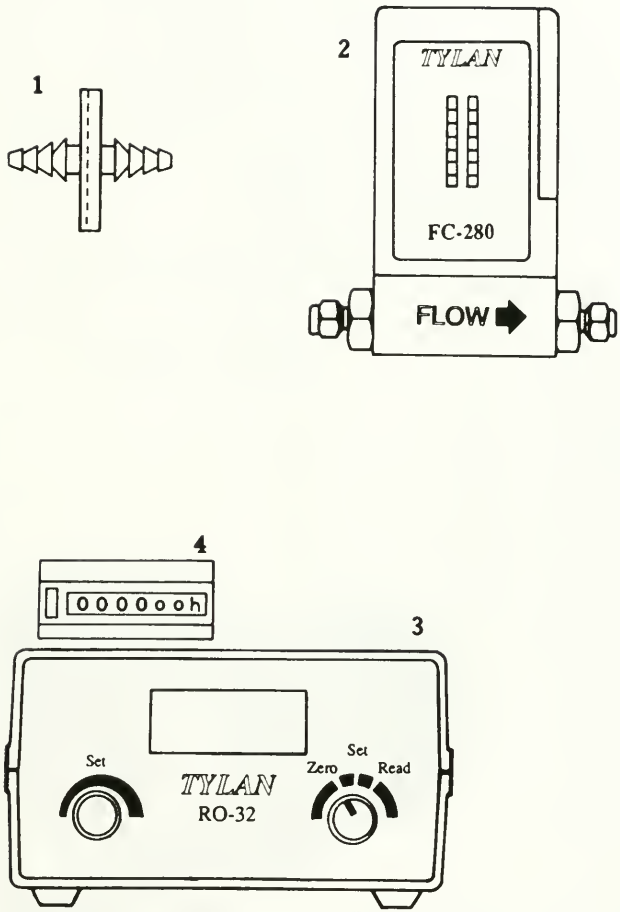
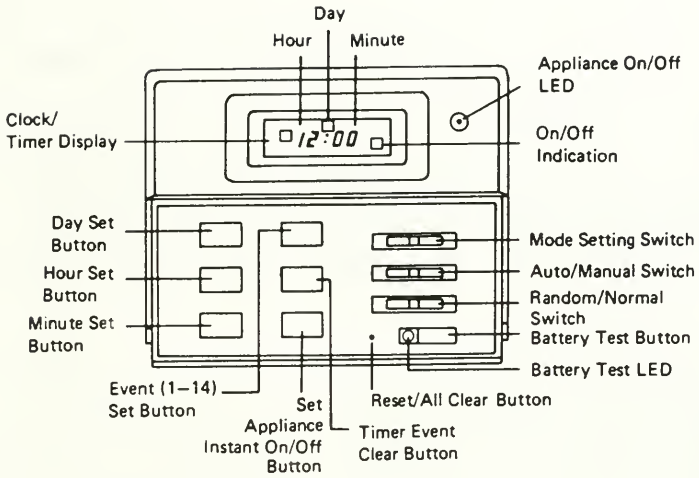


FIGURE 1.3. FILTER[1] / FLOW CONTROLLER[2] / DIGITAL READOUT[3] / ELAPSED TIME INDICATOR[4]



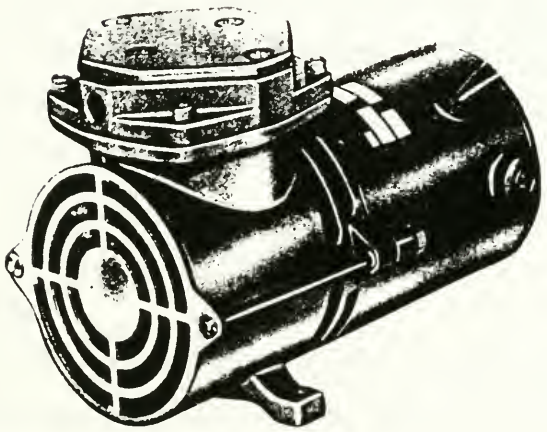


FIGURE 1.4. PROGRAMMABLE TIMER / PUMP

2.0 OPERATION OF THE VOC SAMPLER

2.1 Sampler Set-Up Prior to Sample Collection

This section describes the procedures to follow to set the sampler up for the collection of a volatile organic sample.

2.1.1 General

The sampling train set-up is shown in Figure 1.1 (§1). The in-line filter is kept close to the mass flow controller so that it will not interfere with other equipment installed in the sampling manifold. All equipment should be kept neatly together in a convenient spot where waste heat from the sampling pump will not create problems for other samplers at the station. A spare, or "dummy" cartridge should be left installed between sampling periods. When a sample is to be taken the dummy cartridge is removed and the cleaned new cartridge is installed and the timer set. The exact procedure for accomplishing this is described below.

2.1.2 Specific

This section describes how to install a clean cartridge in preparation for taking a VOC sample. Clean cartridges should be removed from the refrigerator one hour before sample change-over so that they may warm up to room temperature before installation.

i) loosen the swagelock fittings at both ends of the dummy cartridge and remove the dummy cartridge.

ii) wearing clean cotton gloves remove the clean cartridge from the glass shipping tube and remove the shipping plugs from both ends of the cartridge. Place the shipping plugs in the glass shipping tube.

iii) place the cartridge in the stainless steel fitting attached to the glass sampling port with the Carbotrap (dark) adsorbent closest to the glass sampling port.

iv) double-check that the dark sorbent is the first to trap sampled air.

v) tighten the swagelock fitting - finger tight ONLY - followed by an eighth turn with a crescent wrench. Over-tightening will crack the cartridge and ruin the sample.

vi) attach the top swagelock fitting to the open end of the cartridge (the light adsorbent will be furthest from the sampling port).

vii) REMEMBER - finger-tight only followed by 1/8th turn with a crescent wrench.

The clean cartridge is now installed ready for sampling. The cotton gloves may now be removed and discarded. The next step in the procedure is to set the timer.

2.1.3 Setting the Timer

Each timer comes with a comprehensive instruction manual which should be read and understood before using the timer. For the sake of convenience, the steps for setting the timer on/off function are repeated here. If there are any problems with the timer the owner's manual should be referred to.

2.1.3.1 Setting the Current Time

i) Clear all previous programs and the current time setting by pushing the Reset button with a small pointed object.

ii) Move the Lock/Program/Timeset switch (Mode Setting switch) to TIMESET.

iii) Use the DAY Set; HOUR Set; and MINUTE Set buttons to adjust the display to show the current time.

iv) Ensure that the AM/PM Indicator in the display window is showing the correct time of day.

v) Move the Mode Setting switch to PROGRAM.

2.1.3.2 Setting the Sampling Time

i) Ensure that the Mode Setting switch is in the PROGRAM position.

ii) The display will show "S" for Sunday; "0:00" for time and "1" for the event.

Odd numbered programs turn the pump on and even numbered programs turn the pump off.

iii) Use the DAY Set; HOUR Set; and MINUTE Set buttons to adjust the display to show the day and time at which sampling is to begin. NOTE - Sampling is from midnight to midnight.

iv) Press the EVENT button once to advance to the second program.

v) Use the DAY Set; HOUR Set; and MINUTE Set buttons to adjust the display to show the day and time at which sampling is to end.

vi) After setting the two programs (1=ON; 2=OFF) move the Mode Setting switch to LOCK.

vii) Ensure that the Random/Normal switch is set to NORMAL.

The sampling on/off function is now set but before leaving the sampler an initial flow rate reading must be taken.

2.1.4 Setting the Flow Rate

The flow rate is set as follows:

i) push the SET button to bypass the timer and turn the pump on.

ii) allow the pump to run for 3-5 minutes so that the flow may stabilize.

iii) using the trim pot on the face plate of the digital readout mass flow meter set the flow to 25 ml/min.

iv) push the SET button to turn the pump off.

All steps are now complete and the sampler will turn on at 00:00 of the desired sampling day, run for 24 hours, and then turn off at 24:00. Steps for removing the exposed sample are detailed below.

2.2 Removal of the Exposed Sample

The exposed sample should be removed as soon as possible after sampling has stopped so as to minimize any passive uptake to or loss from the sample. ***No more than three days should elapse before the sample is removed.*** This should present no problem in most instances except when a sample finishes running at midnight before a four-day weekend; e.g. Easter or over Christmas. Sampling should be re-scheduled in these cases.

The step by step procedure for removing an exposed sample is detailed below.

2.2.1 Preparation

Preparation for removal of the exposed sample consists of ensuring

that all necessary equipment is assembled before going to the site to remove the sample. Required equipment includes:

i) clean cotton gloves

ii) crescent wrench

iii) glass shipping tube with molecular sieve and end plugs for the exposed cartridge

iv) cooler with freeze packs

v) field sheet for recording sample history

2.2.2 Removal of the Exposed Sample

i) undo the upper Swagelock fitting and remove it from the cartridge.

ii) place one of the end caps on the exposed end of the cartridge and tighten it in place - finger tight ONLY - followed by an eighth turn with the crescent wrench.

iii) undo the lower Swagelock fitting.

iv) remove the cartridge and place the second end cap on the exposed end of the cartridge and tighten it in place - finger tight ONLY - followed by an eighth turn with the crescent wrench.

v) place the capped, exposed cartridge in the glass culture tube and screw on the teflon-lined lid. Place the culture tube in the

cooler in one of the holes drilled in the foam liner.

vi) replace the dummy cartridge in the sampling train and tighten the Swagelock fittings. This prevents other equipment at the station from sampling room air.

The exposed cartridge is now ready to be shipped to:

Trace Organics Section
Ministry of the Environment
Laboratory Services Branch
125 Resources Road
Rexdale, Ontario

Exposed cartridges should be shipped to the laboratory as soon as possible so as to minimize sample deterioration prior to analysis.

Before sealing the cooler and shipping it to the laboratory the sample submission/history form must be filled out. Instructions for doing this are detailed in the next section. Once the form is completed it should be placed inside the cooler and the cooler lid taped shut. The cooler may now be shipped to the above address.

3.0 SAMPLE DOCUMENTATION

3.1 The Sample Submission/History Form

A form has been designed to ensure that all pertinent information about the sample is recorded. An example of the form is shown in Figure 3.1. The form combines the following two forms:

i) LIS Sample Submission Form

ii) LIS Request for Analysis Form

and also has additional space so that information that would normally be recorded on a separate field sheet may be included. The top box incorporates fields for all the information contained in the above-mentioned forms. Some of the fields are pre-printed, such as Sample Program Code; Lab; Pri; and the Primary Client Code. A list of valid Field Comment codes is printed on the back of the form.

3.2 Completing the Sample Submission/History Form

3.2.1 Submission Information - The First Box

The top box of the form contains the information previously coded on the LIS Submission Sheet. The fields are filled in as follows:

i) Submission No. - a six character alphanumeric field to be completed by regional personnel. The first two characters indicate the region submitting the sample.

Ministry of the Environment
Ontario

VOLATILE ORGANICS SAMPLING PROGRAM
SAMPLE SUBMISSION/HISTORY FORM

SUBMISSION NO.. _____ SAMPLE PROGRAM CODE: 02 004 02

LAB: TR PRI: N FD TYPE: ____ SAMPLING AGENCY: 01 02 02 05 01 DATE SUBMITTED: ____/____/____

REGION: _____ TELEPHONE: _____ PRIMARY CLIENT CODE: AR019 COPIES TO:_____/_____/_____/_____

FIELD OPERATOR: _____ SUBMITTED BY:_____(print)_____(sign)

FIELD SAMPLE NO	SAMPLE TYPE	LABORATORY SAMPLE NUMBER	SAMPLE DATE ddmmmyy	STATION ID NO	REMARK CODE	TEST GROUP	ELAPSED TIME COUNTER START	ELAPSED TIME COUNTER END	TOTAL MINUTES	FLOW RATE mL/m	VOLUME (L)	FIELD COMMENTS
	VC					PA VOC1 PA VOC2 PA VOC3						

SPECIAL REMARKS:

0380 (05/89 Front) Original to MOE Lab 1 Copy to Program Coordinator 1 Copy to Region

FIGURE 3.1. THE SAMPLE SUBMISSION / HISTORY FORM

ii) Sample Program Code - a seven (7) or nine (9) digit integer representing the program, study, project, and sub-project (if used). Currently the sub-project is not used. This field is pre-printed on the form and will read 02 (Air Assessment and Abatement Program), 004 (Hazardous Contaminants Study), 02 (Volatile Organics Project).

iii) Lab. - this is pre-printed with the code "TR" for Toronto Lab (currently the only valid code).

iv) Priority - this is pre-printed with the code "N" for normal (prior written permission is required for high priority submissions).

v) FD Type - this field is to be left blank.

vi) Sampling Agency - a ten (10) digit number representing the organizational unit responsible for collecting and shipping the samples. The digits are: Ministry (2); Division (2); Branch/Region (2); Section (2); and Unit (2). This field is pre-printed with the code for ARB which is 01 02 02 05 01.

vii) Date Submitted - a six (6) digit integer representing the day, month, and year on which the submission was shipped to the lab. This field is completed by field personnel.

viii) Region - the region in which the sample originated. Short form may be used; e.g. WC for West Central.

ix) Telephone - the telephone number, beginning with the area code, of the region in which the sample originated.

x) Primary Client Code - a five (5) character alphanumeric field. This is pre-printed as AR019 which is the client code for the program coordinator.

xi) Copies To - enter a maximum of four (4) client codes of people wishing to receive copies of the LIS output; e.g. Air Quality Chiefs.

xii) Field Operator - ***print*** the name of the person who actually collected the sample.

xiii) Submitted By - ***print*** the name of the person who actually submitted the sample (i.e. filled out the submission sheet) and then ***sign*** in the space provided.

3.2.2 Request For Analysis and Field Information - The Second Box

The second box on the form contains information previously coded on the LIS Request For Analysis form and also provides space for recording field information pertinent to the history of the collected sample. Instructions for completing this section of the form are detailed below.

i) Field Sample Number - a five (5) digit number assigned by the field operator. Paired numbers are supplied on rolls of self-adhesive labels. One number should be affixed to the field sheet in the space provided and the other should be affixed to the glass culture tube used to ship the sorbent cartridge. ***At no time*** should field sample numbers (or anything else) be affixed to the sorbent cartridge.

ii) Sample Type - a code assigned by the lab. For the volatile organics sampling program the code is VC and this is pre-printed on the form.

iii) Laboratory Sample Number - this is a number assigned by laboratory personnel to keep track of the sample within the lab.

iv) Sample Date - a six (6) digit integer. Numeric day, month, and year on which the sample was taken. Days and months less than 10 should be coded with a preceding zero; e.g. the third of February, 1989 should be coded as 030289. As sampling is on a 24 hour basis there is no need for a sample start date and sample end date format.

v) Station Identification Number - a five (5) digit integer. This number is assigned according to AQUIS protocol. Most VOC sampling sites will be installed at existing AQI sites and will use that station I.D. number.

vi) Remark Code - a field completed by lab personnel to record anything unusual about the sample.

vii) Test Group - the Test Group code is assigned by the lab and is pre-printed on the form as PA VOC1; PA VOC2; and PA VOC3. Three test groups are required to accommodate the number of compounds analyzed.

viii) Elapsed Time Counter - record the reading on the elapsed time counter before sampling starts and again after sampling ends. The counter may be reset before each sampling period so the "start"

reading is always 000000 if so desired.

ix) Total Minutes - a five (5) digit real number representing the total number of minutes that the sampler ran to one (1) decimal place; e.g. if the sampler ran for exactly 24 hours the total minutes would read 1440.0. The number is obtained from the start and end readings on the elapsed time counter.

x) Flow Rate - a three (3) digit number to record the flow rate to one (1) decimal place as shown on the digital read-out for the mass flow controller.

xi) Volume - a four (4) digit number obtained by multiplying the total minutes by the flow rate and then dividing by 1000. For example: the total minutes reads 1441 and the flow rate was 25.1 ml/min, the volume would then be 36,169.1 ml divided by 1000 to yield 36.1691 litres which would be recorded as 36.17.

xii) Field Comments - an alphabetic character used to indicate any unusual sampling conditions. Valid field comment codes are listed on the back of the submission/history sheet. They are;

M- sampler Malfunction or sampling interruption

D - sampling Duration not 24.0 hr +/- 1.0 hr

S - sampling Start time not 00:00 +/- 01:00 hr

I - cartridge broke during Installation

R - cartridge broke during Removal

N - non-NAPS sampling day

L - Local interference

As many codes as necessary may be used in the field comment space. If something affects the sample that is not covered by the listed field comments it may be described in the Special Remarks section (see below).

3.2.3 Special Remarks - The Third Box

The third section of the sample submission/history form is for recording any useful information not covered in the first two sections. The special remarks section may be used to expand on the field comment codes or to note when a sampling pump is changed or that the mass flow controller was re-calibrated, etc. etc.

4.0 CALIBRATION OF THE SAMPLING TRAIN

The mass flow controller is shipped from the supplier calibrated with air for 0-50 ml/min. This calibration is verified at Air Resources Branch before shipping the sampler to the field for use. Periodically, the calibration of the mass flow controller must be checked against a primary standard such as a bubble meter. A five-point calibration (10,20,25,30,40) adequately covers the sampling flow rate.

4.1 Calibration

The following instructions are for checking the calibration of the mass flow controller. It is recommended that a Gilibrator be used (an automated bubble meter) to avoid inaccuracies introduced through the use of a stop-watch and "manual" bubble meter. For more detailed instructions the manuals for the Gilibrator and the mass flow controller should be referred to.

i) Plug the mass flow controller and the Gilibrator into a power source and allow them to warm up for 10-15 minutes.

ii) Set up the sampling train as you would to take a sample and attach the Gilibrator to the outlet of the pump.

iii) Zero the mass flow controller and allow about 1 minute for stabilization.

iv) Set the first flow rate (10 ml/min) on the controller and allow 1-2 minutes for it to stabilize.

v) Obtain 3 consistent readings on the Gilibrator.

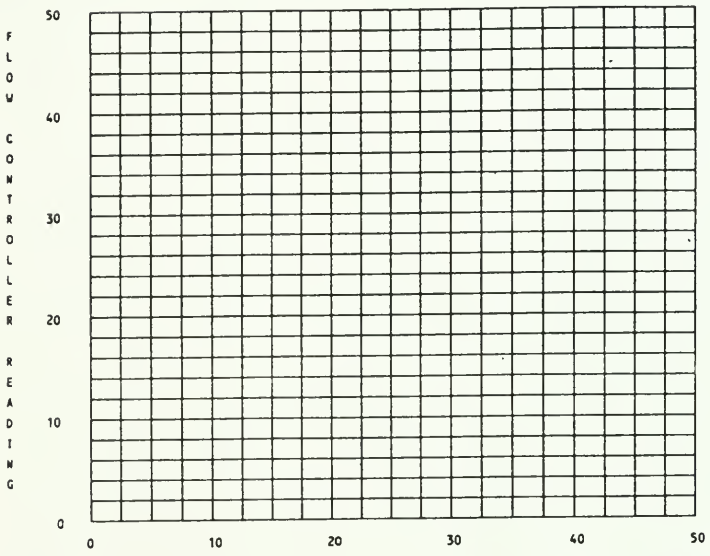
vi) Record both the controller and Gilibrator flow rates.

vii) Repeat steps iv) to vi) for the following flow rates: 20 ml/min; 25 ml/min; 30 ml/min; and 40 ml/min.

Plot the results using the Gilibrator flow rates on the X axis and the mass flow controller readings on the Y axis. If the flow rate indicated by the mass flow controller is within 10% of that indicated by the Gilibrator, no action need be taken. If this is not the case, the gain on the mass flow controller may be adjusted using potentiometer R9. The linearity may be adjusted using potentiometer R19. If the mass flow controller still seems to be out of calibration, adjustment of the bypass valve may be necessary. Refer to the FC-280 Tylan Mass Flow Controller Instruction Manual for detailed instructions on making any adjustments.

Careful records must be kept of calibration dates and any adjustments made to the mass flow controller. A form is available for this purpose (see QA Manual), an example of which is shown on the following page.

MASS FLOW CONTROLLER CALIBRATION FORM



Mass Flow Controller	Gilibrator Reading	Average
10	1) _____	
	2) _____	_____
	3) _____	
20	1) _____	
	2) _____	_____
	3) _____	
25	1) _____	
	2) _____	_____
	3) _____	
30	1) _____	
	2) _____	_____
	3) _____	
40	1) _____	
	2) _____	_____
	3) _____	

Region:_____ Site #:_____ Mass Flow Controller S/N:_____

Gilibrator S/N:_____ Calibrated By:_____

Gain Adjusted? YES NO Linearity Adjusted? YES NO